

1 420 Rec'd PCT/PTO 30 NOV 1999

1 "Method of Producing Water-Soluble Glass Fibres"

2

3 The present invention relates to a method for the
4 production of water soluble glass fibres and glass
5 wool.

6

7 It is known that certain glasses, in which the usual
8 glass former, silicon dioxide, is replaced with
9 phosphorous pentoxide, are soluble in water and body
10 fluids. The rate of dissolution is controlled largely
11 by the addition of glass modifiers such as calcium
12 oxide. In simple terms, the greater the concentration
13 of the modifier the slower the rate of dissolution.
14 The rate of dissolution may range from minutes through
15 to several years.

16

17 Soluble phosphate based glasses which have demonstrated
18 good biocompatibility can incorporate inorganic metals
19 such that a sustained release of the metals can be
20 provided at the wound site. Such materials can also
21 find use in mechanical applications where, for example,
22 slow release of an anti-corrosion agent may be
23 beneficial.

24

25 Certain applications require that the glass is in the

1 form of wool or fibres for mechanical applications such
2 as insulation wool and packaging. Thus, for example,
3 Mohr et al in "Fibre Glass" (Van Norstrand, Reinhold
4 Company, New York 1978) and Jaray in "A New Method of
5 Spinning Glass Fibres" (28th Annual SPI RP/C Institute
6 proceedings 1973, Section 3-A) describe the production
7 of wool and fibres, respectively, from molten glass.
8 The glass fibres can be used for insulation,
9 construction or even communication purposes. Glass
10 wool also finds uses in packaging and insulation
11 applications.

12
13 Normally, glass fibres are produced from molten glass
14 using traditional fibre pulling techniques; whereby
15 filaments of high temperature molten glass (850°-
16 1300°C) are formed into strands and stretched over pull
17 rolls before being collected onto a reel.

18
19 Glass wool formation is similar in that the glass is
20 initially melted in a crucible. The crucible has
21 suitable apertures to allow filaments of glass to flow
22 downwards, which are then "blown" into wool using jets
23 of either steam or compressed air. Alternatively,
24 glass wool can be formed using a flame attenuation
25 process, developed by Owens-Corning Fibreglass
26 Corporation circa 1940. In this process molten glass
27 passes through a bushing stage where primary filaments
28 approximately 1 mm wide are formed. The fibres are
29 then aligned into an exact uniformly juxtaposed array,
30 using a fibre guide, into a jet flame issuing from an
31 internal combustion burner. The jet flame causes
32 thinning and lengthening of the fibres before they are
33 collected on a steel mesh belt.

34
35 In both cases, the glass is either supplied in molten
36 form direct from a crucible or from a temperature-

2

3

12

19

3

35

36 oxides of elements such as lead and tellurium have

1 previously been used in glass as additives to affect
2 qualities of the glass; crystallisation temperature,
3 viscosity and density, for example. As a result of
4 environmental concerns and particularly when the
5 glasses are to be used in a biological application
6 these additives must be avoided and replaced by more
7 acceptable alternatives.

8
9 Therefore, it is an object of the present invention to
10 provide environmentally acceptable water soluble glass
11 fibres with suitable mechanical properties, and to
12 produce said fibres under less forcing conditions.

13
14 The present invention provides a method for forming a
15 water-soluble glass fibre and/or glass wool, the method
16 comprising producing a water-soluble glass and heating
17 said glass above its melting point to form molten
18 glass, cooling at least a portion of said molten glass
19 to a pre-selected working temperature and then
20 processing said molten glass having said working
21 temperature into fibres and/or wool.

22
23 Generally, the glass is initially heated to a melting
24 temperature of 500°-1200°C, preferably 750°-1050°C.
25 The temperature is then slowly lowered to the working
26 temperature at which fibre formation occurs.

27
28 Generally, the working temperature of the glass will be
29 at least 200°C lower than the temperature at which the
30 glass is initially heated. Suitable working
31 temperatures may fall within the following ranges 400°-
32 500°C, 500°-900°C (preferably 550°-700°C, more
33 preferably 550°-650°C, especially 600°-650°C) and 800-
34 1000°C. The working temperature selected will depend
35 upon the glass composition, but an approximate
36 indication of a suitable working temperature can be

094434-1-13090

1 established as hereinafter described. Depending upon
2 the glass composition used, the working temperature may
3 be a range of suitable temperatures. The range of
4 working temperatures may be narrow, for example of only
5 10°C, so that fibre formation may occur only between
6 the temperature of N°C to (N+10)°C. Other glass
7 compositions may have a wider temperature range for the
8 working temperature in which glass formation is
9 possible.

10
11 Alternatively, the working temperature of the glass may
12 be defined as 50-300°C above the T_g of the glass.

13
14 In order to obtain an approximate indication of the
15 working temperature for any particular glass
16 composition, the glass composition should be slowly
17 heated to its melting point. As soon as the glass is
18 molten, frequent attempts to pull the composition
19 upwardly to form a fibre should be made, with the
20 temperature of the composition being very gradually
21 increased between attempts. The temperature range of
22 the composition during which fibre formation is
23 possible should be noted and used as a preliminary
24 working temperature in the process of the invention.

25
26 It will be clear to those skilled in the art that the
27 pulling speed at which the fibre is drawn off can
28 affect the choice of working temperature and the
29 diameter of the fibre required. Where a fibre of
30 relatively large diameter is required, the fibre tends
31 to be pulled more slowly and the working temperature
32 may need to be decreased slightly. Where a fibre of
33 relatively small diameter is required (eg a glass
34 wool), the fibres may be drawn at the much higher
35 pulling speed and the working temperature may need to
36 be increased (thus lowering the viscosity of the

09444341.1306

1 composition to accommodate the increased pulling
2 speed). Selection of the exact working temperature in
3 respect of any particular fibre size and composition
4 will be a simple matter of routine evaluation of
5 optimal process conditions.

6
7 With reference to the "working temperature" of the
8 glass, the skilled person will appreciate that the
9 furnace temperature may differ considerably from the
10 temperature of the glass itself and indeed there may be
11 a significant temperature gradient in the glass.
12 Ideally the "working temperature" will be the
13 temperature of the glass as fibre formation (ie.
14 pulling) takes place. In many compositions however, it
15 may not be practical to measure the temperature at the
16 surface of the glass where pulling occurs by insertion
17 of a temperature probe as the introduction of the probe
18 may precipitate crystallisation of the glass. One
19 alternative is to place a temperature probe into the
20 bushing and to monitor the bushing temperature which
21 will be a good indicator of the glass temperature at
22 the moment of fibre formation. Alternatively an Infra
23 Red pyrometer may be focused onto the appropriate area
24 of the glass and used to monitor the temperature.

25
26 The glass to be formed into fibres will generally be
27 heated until molten, optionally clarified, and then
28 cooled slowly and controllably until the appropriate
29 working temperature is reached and fibre formation can
30 commence. The initial heating of the glass above its
31 melting point and the subsequent fibre formation may be
32 carried out in a single vessel or, alternatively, the
33 molten glass may be transferred to a vessel designed
34 specifically for fibre formation. One way of holding
35 the molten glass in a vessel having a bushing within
36 its lower surface until the temperature drops to the

004431 1303

1 required working temperature is to coat or fill the
2 holes of the bushing with a material that gradually
3 melts over the period of time taken for the glass to
4 reach the temperature required.

5
6 The most important aspect of the present invention is
7 the manner in which the working temperature is reached.
8 We have found that the molten glass, which may
9 preferably be heated significantly above its melting
10 point, should be allowed to cool in a highly controlled
11 manner, the temperature being only gradually reduced
12 until the working temperature is reached. A stirrer
13 may be present to ensure that the temperature of the
14 whole of the molten glass is kept as uniform as
15 possible.

16
17 The glass is cooled to a temperature at which the glass
18 will not crystallise for at least the period of time
19 needed to convert the melt to fibre. This temperature
20 is termed a "holding temperature". The rate of cooling
21 from this holding temperature is determined by the rate
22 at which the melt is consumed at the bushing and the
23 difference in temperature between the bushing
24 temperature (the working temperature) and the melt
25 holding temperature.

26
27 Due to low viscosity and narrow temperature band for
28 many of these compositions, control of the balance
29 between melt temperature, bushing temperature and glass
30 throughput rate is critical.

31
32 According to a further aspect of the present invention
33 there is provided a composition suitable for processing
34 into glass fibres and/or wool.

35
36 Phosphorous pentoxide (P_2O_5) is preferably used as the

094434 13466

2

3

€

10

1

1

1 glass. By suitable adjustment of the glass
2 composition, the dissolution rates in water at 38°C
3 ranging from substantially zero to 25mg/cm²/hour or more
4 can be designed. However, the most desirable
5 dissolution rate R of the glass is between 0.01 and
6 2.0mg/cm²/hour.

7
8 The water-soluble glass is preferably a phosphate
9 glass, and preferably comprises a source of silver ions
10 which may advantageously be introduced during
11 manufacture as silver orthophosphate (Ag₃PO₄). The
12 glass preferably enables controlled release of silver
13 and other constituents in the glass and the content of
14 these additives can vary in accordance with conditions
15 of use and desired rates of release, the content of
16 silver generally being up to 5 mole %. While we are
17 following convention in describing the composition of
18 the glass in terms of the mole % of oxides, of halides
19 and of sulphate ions, this is not intended to imply
20 that such chemical species are present in the glass nor
21 that they are used for the batch for the preparation of
22 the glass.

23
24 The optimum rate of release of silver ions into an
25 aqueous environment may be selected by circumstances
26 and particularly by the specific function of the
27 released silver. The invention provides a means of
28 delivering silver ions to an aqueous medium at a rate
29 which will maintain a concentration of silver ions in
30 said aqueous medium of not less than 0.01 parts per
31 million and not greater than 10 parts per million. In
32 some cases, the required rate of release may be such
33 that all of the silver added to the system is released
34 in a short period of hours or days and in other
35 applications it may be that the total silver be
36 released slowly at a substantially uniform rate over a

1 period extending to months or even years. In
2 particular cases there may be additional requirements,
3 for example it may be desirable that no residue remains
4 after the source of the silver ions is exhausted or, in
5 other cases, where the silver is made available it will
6 be desirable that any materials, other than the silver
7 itself, which are simultaneously released should be
8 physiologically harmless. In yet other cases, it may
9 be necessary to ensure that the pH of the resulting
10 solution does not fall outside defined limits.

11
12 Generally, the mole percentage of these additives in
13 the glass is less than 25%, preferably less than 10%.

14
15 Embodiments of the invention will be described with
16 reference to the following non-limiting examples.

17

18 **Example 1**

19	Component	Mole %
20	Glass Composition	
21	Na ₂ O	31.05
22	CaO	16.00
23	Ag ₂ O	3.88
24	P ₂ O ₅	46.08
25	Na ₂ PO ₃ F	0.97
26	2Al ₂ O ₃ .B ₂ O ₃	2.00

27

28 100 grams of the sample was heated to 900°C before
29 being cooled and pulled at 650°C, at 25 km/hr. Overall
30 the fibre was good; one sample was 10 km in length and
31 11 grams in weight, although there was some
32 crystallisation at the pulling temperature.

33

34

0942461-13099

1 **Example 2**

2		Component	Mole %
3	Glass Composition		
4		Na ₂ O	29.51
5		CaO	15.21
6		Ag ₂ O	3.68
7		P ₂ O ₅	43.80
8		2Al ₂ O ₃ ·B ₂ O ₃	1.90
9		Na ₂ PO ₃ F	1.90
10		Na ₂ B ₄ O ₇ ·10H ₂ O	1.00
11		Na ₂ PO ₄	3.00

12

13 74 grams of the sample was heated to 1000°C before

14 being cooled and pulled at 635°C at 25 km/hr. The

15 fibre produced was ultrafine; one sample was 18 km in

16 length and 59 grams in weight. The sample was sprayed

17 with WD40 to prevent water absorption and to aid

18 lubricity. There was some debris at the bottom of the

19 crucible, but this was found to be just iron deposits

20 from the brushing rod.

21

22 **Example 3**

23		Component	Mole %
24	Glass Composition		
25		Na ₂ O	34.20
26		CaO	16.15
27		P ₂ O ₅	44.65
28		Na ₂ SO ₄	5.00

29

30

31 200 grams of the sample was heated to 1050°C before

32 being cooled and pulled at 635°C at 25 km/hr. The

33 fibre was good although there was some crystallisation

34 at the pulling temperature.

35

36

1 Example 4

2

3

4 Glass Composition

5

6

7

8

9

10

11

12 117 grams of the sample was heated to 950°C before
13 being cooled and pulled at 635°C, at 40 km/hr. The
14 fibre produced was good and there were no
15 crystallisation problems even though the surface
16 temperature of the fibre dropped to 510°C in the
17 pulling process.

18

19 Example 5

20

21

22 Glass Composition

23

24

25

26

27

28

29

30 99 grams of the sample was heated to 800°C before being
31 cooled to 650°C and pulled at 40 km/hr. The fibre
32 produced was very fine but difficult to pull and quite
33 fragile at speed.

34

35

36

Component

Mole %

 Na_2O

32.40

 CaO

15.30

 P_2O_5

42.30

 $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$

3.00

 $\text{Na}_2\text{PO}_3\text{F}$

1.00

 Na_2SO_4

6.00

Component

Mole %

 Na_2O

31.71

 CaO

14.73

 P_2O_5

36.33

 B_2O_3

4.78

 SO_3

9.40

 $\text{Na}_2\text{PO}_3\text{F}$

3.00

1 **Example 6**

2

3

4

5 Glass Composition

6

7

8



10

11

12

13

14

15

15
16 200 grams of the sample was heated to 850°C before
17 being cooled to 545°C and pulled at 40 km/hr. The
18 fibre produced was strong and thin; there was not a
19 problem of crystallisation, in fact the glass can be
20 stored at 550°C for 72 hours without the onset of
21 crystallisation.

200 grams of the sample was being cooled to 545°C and pulled at 40 km/hr. The fibre produced was strong and thin; there was not a problem of crystallisation, in fact the glass can be stored at 550°C for 72 hours without the onset of crystallisation.

17 being cooled to 545 °C and for
18 fibre produced was strong and thin; there was not a
19 problem of crystallisation, in fact the glass can be
20 stored at 550°C for 72 hours without the onset of
21 crystallisation.

18 fibre produced was strong and clear,
19 problem of crystallisation, in fact the glass can be
20 stored at 550°C for 72 hours without the onset of
21 crystallisation.

19 problem of crystallisation, in fact the
20 stored at 550°C for 72 hours without the onset of
21 crystallisation.

21 crystallisation.

2

23 Example 7

23 Example 7
24 Below is an example of a wool formulation and running
25 conditions to illustrate the differences with the
26 monofilament examples given above.

24 Below is an example of
25 conditions to illustrate the differences with the
26 monofilament examples given above.

26 monofilament examples given above.

2

28 A typical wool formulation is

2

30	Na ₂ O	26.31
----	-------------------	-------

31	CaO	17.78
----	-----	-------

32	P ₂ O ₅	47.04
----	-------------------------------	-------

33	B ₂ O ₃	5.94
----	-------------------------------	------

34	MnO	1.55
----	-----	------

35	Fe_2O_3	0.97
----	-------------------------	------

36	NaF	0.41
----	-----	------

37
38 Solution rate, non annealed = 0.0278 mg.cm⁻²hr⁻¹

1 Melted and refined at 1000°C.
2 Cooled and held at 725°C.
3 Bushing temperature maintained at 365°C.
4
5 Thick fibres approx 1.2mm diameter drawn through pinch
6 rollers at 2.5 M.mm⁻¹ from a bushing with 6 x 6.5mm
7 diameter holes. Fibres jet attenuated to produce a
8 fine wool 5 -15µm diameter. The wool was sprayed with
9 silicone oil finish during the attenuation process and
10 collected on a stainless steel mesh conveyor.
11 Typically, attenuated wools will have diameters of 5 to
12 20µm. Monofilament fibres will mostly be 20 to 50µm
13 diameter.
14

15 **Example 8**

16	Na ₂ O	31.19 mole %
17	K ₂ O	9.63 mole %
18	Ag ₂ O	2.9 mole %
19	B ₂ O ₃	2.74 mole %
20	2NaF	0.66 mole %
21	P ₂ O ₅	52.88 mole %

22 Furnace at 710°C - 800°C.

23 Bushing at 450°C - 460°C.

24 4.5mm bushing holes.

25 50km per hour pull rate.

26 Good fibres.

27 Solution rate = 1.68 not annealed 2.28 annealed.

28

29 **Example 9**

30	Na ₂ O	32 mole %
31	K ₂ O	10 mole %
32	Ag ₂ O	3 mole %
33	P ₂ O ₅	55 mole %

34

35

36

37

38

660ET "T842460

- 1 Furnace at 850°C.
- 2 Bushing at 530°C.
- 3 5mm bushing holes.
- 4 55kmph.
- 5 Good strong fibres.

6

7 **Example 10**

- | | | | |
|----|-------------------------------|-----------|------------------------------|
| 8 | Na ₂ O | 32 mole % | |
| 9 | K ₂ O | 10 mole % | |
| 10 | (MgO | 4 mole %) | - added as an anti-microbial |
| 11 | B ₂ O ₃ | 5 mole % | |
| 12 | Ag ₂ O | 3 mole % | |
| 13 | P ₂ O ₅ | 46 mole % | |
- 14
- 15 Furnace temperature 650°C - 730°C.
 - 16 Bushing temperature 410°C - 420°C.
 - 17 Bushing 5.5mm diameter.
 - 18 Speed up to 100kmph.
 - 19 Solution rate 0.7 annealed 1.0 non annealed (mg.cm⁻³.hr⁻¹).
 - 20 Very good strong reliable fibre. Very stable.

21

22 **Example 11**

- | | | | |
|----|-------------------------------|--------------|-----------------------------|
| 23 | Na ₂ O | 36.68 mole % | |
| 24 | K ₂ O | 8.63 mole % | |
| 25 | P ₂ O ₅ | 45.09 mole % | |
| 26 | B ₂ O ₃ | 5.29 mole % | |
| 27 | Ag ₂ O | 2.59 mole % | |
| 28 | (CaO | 1.73 mole % | to attenuate solution rate! |

29

- 30 Furnace temperature 550°C.
- 31 Bushing 62 x 5.0mm holes.
- 32 Bushing temperature 400°C.
- 33 Speed 80kmph.
- 34 Very good fibres.
- 35 Solution rate 3.11 annealed, 3.8 non annealed (mg.cm⁻².hr⁻¹).
- 36
- 37 The fibres show excellent tensile strength, flexibility
- 38 and shock resistance.

1 The fibres are especially suitable for industrial and
2 plastics reinforcement controlled release (anti-
3 microbial, anti-corrosion etc) and rapidly
4 biodegradable applications.
5

6 **Example 12**

7 CaO 30 mole %
8 MgO 20 mole %
9 P₂O₅ 50 mole %

10

11 Furnace at 1050°C.
12 Bushing 5.5mm holes.
13 Bushing temperature 700°C - 720°C.
14 Speed up to 80kmph.
15 Solution rate TBA.
16 Very strong fibre.

17

18 **Example 13**

19 (K₂O 5 mole %) Trace to alter dissolution rate
20 CaO 25 mole %
21 Mg₂O 20 mole %
22 P₂O₅ 50 mole %

23

24 Furnace 1000°C.
25 Bushing 5.5mm.
26 Bushing temperature 560°C - 620°C.
27 Speed up to 70kmph.
28 Solution rate TBA.
29 Very strong fibre.
30 Anti-microbial.

31

32 **Example 14**

33 CaO 28.5 mole %
34 MgO 18.5 mole %
35 Ag₂O 3 mole %
36 P₂O₅ 50 mole %

37

38

66057-1300

- 1 Furnace temperature 1050°C - 1150°C.
- 2 Bushing 4 x 5.5mm.
- 3 Bushing temperature 700°C.
- 4 Speed 50kmph.
- 5 Solution rate TBA.
- 6 Very good, strong fibre.
- 7 Anti-microbial.

8

9 **Example 15**

- | | | |
|----|-------------------------------|-----------|
| 10 | CaO | 30 mole % |
| 11 | MgO | 20 mole % |
| 12 | P ₂ O ₅ | 50 mole % |

13

14 As Example 14 (without silver)

15

16 The fibres show excellent tensile strength, flexibility
17 and shock resistance. These fibres are suitable for
18 applications requiring slower release and greater
19 tensile strength plus biodegradability. The fibres are
20 suitable for orthopaedic implants and tissue
21 engineering applications.

22

23

24

05061113460